Determination of Paraquat Residues in Food Crops by Gas Chromatography

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The herbicide paraquat (1,1'-dimethyl-4,4'-bipyridylium ion) has been used as the dichloride or bis (methyl sulfate) salt for weed control in many crops and non-crop areas, defoliation, desiccation, and chemical seed bed preparation. Although, paraquat is considered essentially biologically inactive in most soils, root uptake of the herbicide have been reported from soils if it is leached into the root zone of plants (COATS et al. 1965, DAMANAKIS et al. 1970). Residues of paraquat may also be expected in certain crops that receive direct spray of the herbicide or when it is used as a dessicant (ASHTON and CRAFTS 1973). Therefore, a reliable and sensitive method for determining residues of paraquat in plant material is desirable. CALDERBANK and YUEN (1965) described an ion-exchange procedure for determining paraquat residues in fruits and in a wide variety of food crops. This method, however, involves a time consuming ion-exchange step and is likely subject to interferences from certain naturally occuring plant substances in the colorimetric determination. Furthermore, certain reduced bipyridylium compounds may not follow Beer's law in aqueous solution (CORWIN et al. 1968).

SODERQUIST and CROSBY (1972) determined paraquat in water by its catalytic hydrogenation and subsequent analysis by gas chromatography using a flame ionization detector. Their attempts to apply this procedure to crop materials were unsuccessful as no recovery of paraquat added at 1.0 ppm level were obtained. Recently, we reported a procedure for determination of diquat and paraquat residues in soil by gas chromatography (KHAN 1974). The method involves catalytic hydrogenation of the acid extract of soil, extraction of the material into organic solvents and analysis by gas chromatography. In this paper we report the modified procedure developed for paraquat residues determination in lettuce, carrots and onions.

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Materials and Methods

Chemicals. All solvents were pesticide grade and used as received. Analytically pure paraquat dichloride was supplied by Chevron Chemical Co., Richmond, Calif. Platinum oxide (Adam's catalyst) was purchased from Matheson Coleman and Bell Inc., Norwood, Ohio.

Sampling. Representative samples of lettuce, carrots and onions were taken from fields which had not been previously treated with paraquat. The tops and roots of carrots and onions were separated and the tops discarded. The samples were washed with cold water to remove any adhearing soil particles. Each lettuce or onion was cut into four equal segments resulting in four subsamples. One subsample was diced into small pieces (approximately 1-cm square), mixed thoroughly, and about a 0.5 Kg aliquot was retained for analysis. About 1 Kg of carrots taken at random from the bulk sample was diced into small pieces, mixed thoroughly, ground in a blender and a 0.5 Kg aliquot was retained for analysis.

Determiniation of Residues in Lettuce, Carrots and Onions Fortified with Paraquat. Lettuce, carrots and onions were fortified with paraquat at the 0.5-, 0.1- and 0.05- ppm levels using 50 g of sample in a 300-ml boiling flask. The sample was then mixed with 80 ml of 5N H_2SO_4, a few drops of octane -2-ol, and refluxed for 5 hr. The content of the flask was swirled occasionally to prevent local overheating and charring until the solution started boiling steadily. The extract was filtered under suction through an acid resistant filter paper. The boiling flask and sample residue on the filter paper were washed successively with several small portions of distilled water. The acid extract was introduced into a hydrogenation flask containing 150 mg of PtO_2. The procedure for hydrogenation and extraction of the hydrogeneted material into hexane was essentially the same as that described earlier (KHAN 1974). The hexane layer was concentrated to about 1 ml with a gentle stream of dry air. The material was quantitatively transferred on top of an alumina column (2 cm diameter, 3 g aluminum oxide W200 basic, Woelm, activity I, previously washed with 50 ml of 30% acetone in hexane) and eluted with 250 ml of 30% acetone in hexane. No paraquat was eluted by this eluate. The column was then eluted with 150 ml of methanol and the collected eluant was concentrated to about 10 ml under reduced pressure at room temperature on a rotating evaporator. Finally, the methanol was removed with a gentle stream of dry air, residue dissolved in hexane and analyzed by gas chromatography.

Gas Chromatography. The gas chromatograph used was a Pye Series 104, Model 124, fitted with an alkali flame ionization detector having a CsBr Annulus. The chromatographic column was 1.5 m x 0.6 cm glass tube packed with 3% Carbowax 20M + 1% KOH

coated on 80-100 mesh Chromosorb WHP. The column, detector, and injector temperatures were 150°C, 200°C and 150°C, respectively. The carrier gas, nitrogen, flow rate was 55 ml/min, while those of hydrogen and air were 40 and 400 ml/min, respectively. Under these conditions, the retention time of paraquat was 1.8 min. The amount of paraquat in a sample was determined by comparing its peak height with that of the hydrogenated standard and correcting the value for the change in molecular weight on hydrogenation.

All samples were analyzed in triplicate and average values are reported. All residue data are reported on fresh weight basis.

Results and Discussion

The control check samples of lettuce, carrots and onions exhibited a peak that had retention time very similar to paraquat (Fig. 1a). Presence of this interfering substance complicated quantitative analysis of paraquat residues in the samples. However, alumina column cleanup removed this interfering peak from the samples (Fig. 1b). The first eluting solvent (30% acetone in hexane) also removed some of the other coextracted peaks. A comparison of the chromatograms with and without cleanup demonstrate the effectivenss of the alumina column cleanup procedure used in this study. Preliminary experiments showed that 91.8 (±2.2)[1]% of the hydrogenated reference standard was recovered from the column by eluting with methanol. Fig. 1c show the chromatograms of fortified samples that had been subjected to the cleanup procedure.

Average percentage recoveries of paraquat from lettuce, carrots and onions, fortified with known amounts of this compound at three different levels, were between 75 and 86, with maximum standard error of 4% (Table 1). It can be seen that the method was capable producing good recoveries and has the sensitivity of 0.05 ppm. Since the interference from coextractives was nearly negligible after the alumina column cleanup, an improved sensitivity may be obtained by concentrating the final solution to a smaller volume without any significant interferring background.

The residue method developed for paraquat may also be applicable to other crops. The technique of cleanup and analysis described in this paper, is reasonably simple to perform and an analyst should be able to use it with no difficulty.

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[1] Numbers in parenthesis show the standard error of the mean.

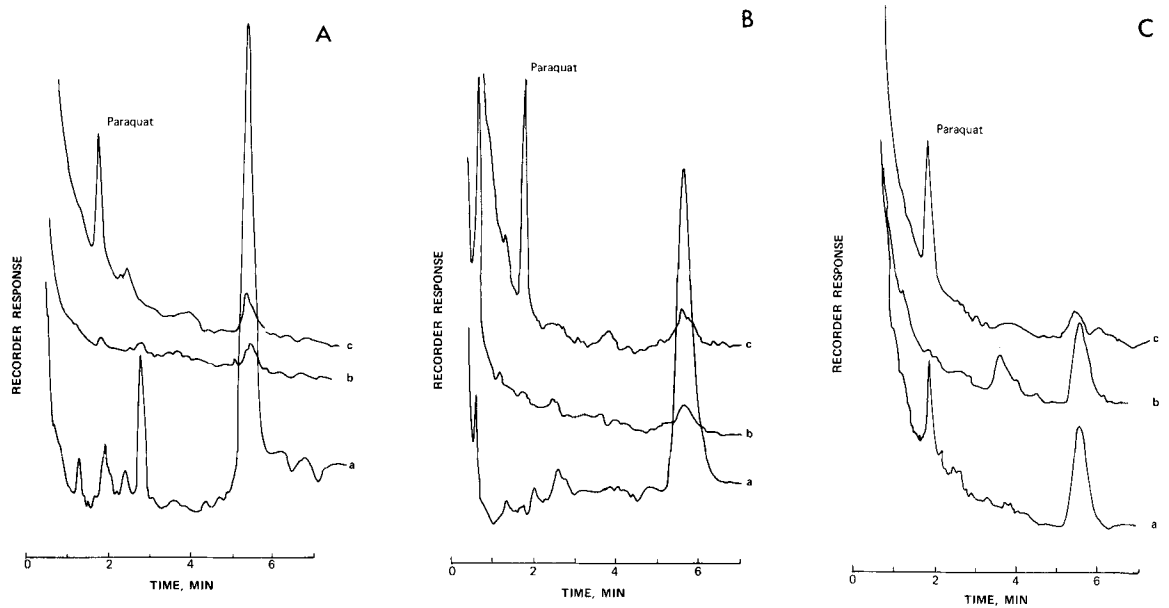

Fig. 1. Gas chromatograms from determination of paraquat residue in fortified (A) lettuce, (B) carrots, and (C) onions. GC conditions: glass column, 1.5 m x 0.6 cm with 3% Carbowax 20 M + 1% KOH on chromosorb WHP; column, detector, and injector temperatures 150°C, 200°C and 150°C, respectively; nitrogen carrier flow 55 ml/min; hydrogen flow 40 ml/min; air flow 420 ml/min; attenuation 20 x 1; and chart speed 1.25 cm/min. (a) control check without column cleanup, (b) control check after column cleanup, and (c) fortified sample (0.05 ppm) after column cleanup.

TABLE 1

Recovery of paraquat from fortified lettuce, carrots and onions (mean value for triplicate samples with standard errors).

Crop	Paraquat added ppm	Recovery %
Lettuce	0.5	85.9 ± 4.0
	0.1	78.4 ± 1.0
	0.05	74.9 ± 1.0
Carrots	0.5	80.4 ± 2.0
	0.1	79.4 ± 3.0
	0.05	75.3 ± 1.9
Onions	0.5	78.1 ± 1.6
	0.1	80.6 ± 2.3
	0.05	76.9 ± 2.5

Summary

A method is described for determining paraquat residues in lettuce, carrots and onions. The procedure is based on the extraction of the sample with 5N H_2SO_4 and catalytic hydrogenation of the acid extract. This is followed by column cleanup on alumina and subsequent determination by gas chromatography. Recoveries of paraquat added to lettuce, carrots and onion at 0.5, 0.1, and 0.05 ppm were between 75 to 86%, with maximum standard error of 4%. The lower limit of this method is in the 0.05 ppm range.

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